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uncertainty, with the values which hold between the same metals at ordinary temperatures.

So far then as experiment has thus far gone, Einstein's equation seems to be an exact statement of the energies of emission of corpuscles under the influence of light waves.

Nevertheless the physical theory which gave rise to it seems to me to be wholly untenable. Be this as it may, however, the photo-electric results herewith presented constitute the best evidence thus far found for the correctness of the fundamental assumption of quantum theory, namely, the discontinuous or explosive emission of energy by electronic oscillators. They furnish the most direct and most tangible evidence which we yet have for the actual physical reality of Planck's *h*.

[1] R. A. Millikan, *Physic. Rev..* Ser. 2, **4**, 73 (1914); *Ibid.*, **6**, 55 (1915).

[2] Einstein, *Ann. Physik.*, Ser. 4, **17**, 132 (1905) and **20**, 199 (1906).

[3] Ramsauer, *Ann. Physik.*, **45**, 1120 (1914), also **45**, 961.

[4] Millikan and Winchester, *Physic. Rev.*, **24**, 16 (1906), and *Phil. Mag.*, Ser. 6, **14**, 188 (1907).

[5] Millikan, *Physic. Rev.* **2**, 143 (1913).

[6] Schottky, *Ann. Physik.*, **44**, 1011 (1914).

THE CHEMICAL ACTIVITY OF THE IONS OF HYDROCHLORIC ACID DETERMINED BY ELECTROMOTIVE FORCE MEASUREMENTS

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The fact that the laws of perfect solutions which are conformed to by unionized or slightly ionized substances in dilute aqueous solutions are subject to large deviations in the case of largely ionized substances (salts, strong acids and bases) even at small concentrations makes it necessary, in the absence of any theoretical explanation of the deviations, to treat dilute solutions of these substances like concentrated solutions of other substances, namely, to determine experimentally the behavior of the separate substances, with the hope that this empirical study may then lead to generalizations. Now the most important characteristic of ionizing substances is the chemical activity which results from their ionization, or more specifically the (mass-action) effect which their ions exercise in determining chemical equilibria. This effect in the case of theoretically perfect solutes is proportional to the concentration of the ions; but in the case of deviating solutes there must be substituted

for it a new quantity, which may be regarded as the 'effective ion-concentration' and which has been appropriately called by Lewis[1] the activity of the ions. This quantity has been shown by Lewis to be thermodynamically related to various other properties of solutions, thereby on the one hand increasing its practical significance and on the other affording independent means of evaluating it.

The most general of these thermodynamic relations, one indeed which may well be regarded as the best practical definition of activity, is that afforded by the equation $F_1 - F_2 = R T \log (a_1/a_2)$ in which R is the perfect-gas constant and $F_1 - F_2$ represents the decrease in the free-energy of the system attending the transfer at the absolute temperature T of one mol of any substance (thus of an ion) from a solution of any concentration in which its activity is a_1 to another solution of any concentration in which its activity is a_2; the free-energy decrease being defined in general to be equal to the maximum work W producible by the change in the state of the system under consideration diminished by the attendant increase in the product of its volume and pressure (that is, $F_1 - F_2 = W - (p_2v_2 - p_1v_1)$).

The most direct way of determining the free-energy-decrease attending the transfer of ions from one concentration to another, and thereby of determining their relative activities, is the measurement of the electromotive force of cells in which such a transfer takes place; and it is with such a study of the ions of hydrochloric acid that this investigation deals. Namely, measurements have been made of the electromotive force at 18, 25, and 35° of cells of the form H_2 (1 atm.), HCl (at various concentrations), Hg_2Cl_2 (solid) + Hg. If two such cells are considered to be placed in series in opposition to each other, the changes at the electrodes of the two cells compensate each other, and the net change in state when one faraday (F coulombs) of electricity passes through it is the transfer of 1 HCl or of 1 H^+ and 1 Cl^- from one solution to the other. Considering the ions, we have therefore the relation:

$$(E_2 - E_1) \text{ F} = F_1 - F_2 = 2 \text{ RT} \log (a_1/a_2),$$

in which $E_2 - E_1$ is the difference in the electromotive force of two cells in which the acid has the free-energies F_2 and F_1 and its ions have the activities a_2 and a_1, respectively. For a_2 and a_1 we may substitute $\alpha_2 c_2$ and $\alpha_1 c_1$ in which α_2 and α_1 are activity-coefficients (analogous to ionization-coefficients) representing the factors by which the concentrations c_2 and c_1 of the acid must be multiplied to give the activities of the ions.

The mean corrected values of the observed electromotive force in

volts and the values of the free-energy-decrease in joules calculated from them by the equation $F_1 - F_2 = 96500 E \times 4.182$ are given in Table 1. These electromotive forces are probably not in error in any case by as much as 0.1 millivolt. The free-energy-decrease is that attending the cell-reaction $\frac{1}{2} H_2$ (1 atm.) $+ \frac{1}{2} Hg_2Cl_2$ (solid) $= Hg$ (liquid) $+ H^+Cl^-$ (at concentration c). The table also contains the values of the increase $(H_2 - H_1)$ in the heat-content of the cell when this reaction takes place at 25°, calculated by the fundamental thermodynamic equation:

$$\frac{H_2 - H_1}{T^2} dT = d\left(\frac{F_1 - F_2}{T}\right).$$

TABLE 1

ENERGY-EFFECTS RELATING TO THE REACTION
$\frac{1}{2} H_2$ (1 ATM.) $+ \frac{1}{2} Hg_2Cl_2 = Hg+HCl$ (AT VARIOUS CONCENTRATIONS).

MOLS HCl PER 1000 G. WATER	ELECTROMOTIVE FORCE AT			FREE-ENERGY DECREASE AT			HEAT DECREASE AT 25
	18°	25°	35°	18°	25°	35°	
4.484	0.15759	0.15506	0.15124	15208	14964	14595	25590
1.9278	0.23769	0.23589	0.23304	22937	22764	22489	30480
1.0381	0.27919	0.27802	0.27595	26942	26829	26629	32130
0.7714	0.29654	0.29571	0.29411	28616	28536	28381	32450
0.5095	0.31912	0.31865	0.31765	30795	30750	30654	33070
0.3376	0.33845	0.33836	0.33794	32661	32652	32611	33380
0.1004	0.39764	0.39884	0.40013	38373	38489	38612	34060
0.0333	0.45020	0.45258	0.45557	43444	43674	43963	34370

In Table 2 are given the corresponding values of the free energy of transfer and heat of transfer of 1 HCl from solutions of various concentrations to a solution of the concentration 0.1000 mols HCl per 1000 g. water. These are obtained from the values of Table 1 by direct subtraction (after reducing the values at the concentration 0.1004 so as to correspond to the round concentration 0.1000). In the table are included also values of the free energy of transfer at 18° for concentrations below 0.0333 molal, these having been calculated from Jahn's[2] measurements of the electromotive force of concentration-cells of the type $Ag+AgCl$, HCl (c_1), $HCl(c_2)$, $AgCl+Ag$. In the next to last column of the table are given the corresponding values of the activity-coefficients at 18°, calculated by the equation given above on the assumption that at the smallest concentration (0.00167 molal) the activity-coefficient is equal to the ionization-coefficient (0.988) derived from the ratio of the equivalent conductance at that concentration to that extrapolated for zero concentration. The last column of the table gives the values

of this conductance-ratio at 18° at the other concentrations, enabling a comparison of it to be made with the values of the activity-coefficient.

It will be seen from Table 2 that with increasing concentration the activity-coefficient first falls more rapidly than the conductance-ratio, being about 10% smaller than the latter at concentrations 0.1 to 0.5 molal. This shows that at these concentrations there is an error of this magnitude in the common practice of employing in mass-action expressions the conductance-ratio as a measure of the activity of the ions of the acid. The activity-coefficient, moreover, unlike the conductance-ratio, passes through a minimum at about 0.50 molal, and then increases rapidly with the concentration, becoming about equal to that

TABLE 2

ENERGY-EFFECTS ATTENDING THE TRANSFER OF HYDROCHLORIC ACID AND VALUE OF ITS ACTIVITY-COEFFICIENT

MOLS HCl PER 1000 G. WATER	FREE-ENERGY DECREASE AT			HEAT DECREASE AT 25°	ACTIVITY-COEFFICIENT AT 18°	CONDUCTANCE-RATIO AT 18°
	18°	25°	35°			
4.484	23184	23544	24037	8474	2.23	....
1.9278	15454	15744	16143	3591	1.063	....
1.0381	11449	11679	12003	1937	0.864	0.841
0.7714	9775	9971	10250	1619	0.823	0.868
0.5095	7596	7757	7978	999	0.795	0.889
0.3376	5730	5856	6021	684	0.816	0.901
0.1000	0	0	0	0	0.844	0.925
0.03332	−5053	−5167	−5331	−300	0.892	0.955
0.01668	−8224	....	....	....	0.926	0.966
0.01115	−10084	....	....	....	0.943	0.971
0.008324	−11447	....	....	....	0.953	0.976
0.006683	−12472	....	....	....	0.960	0.978
0.005569	−13325	....	....	....	0.967	0.980
0.003334	−15717	....	....	....	0.985	0.985
0.001667	−19031	....	....	....	0.988	0.988

ratio at 1 molal, and attaining at 4.5 molal a value $2\frac{1}{4}$ times as great as that at zero concentration. This large increase is in correspondence with the rapid increase of the vapor-pressure of the acid at high concentrations.

Other exact electromotive force investigations from which ion-activities can be derived have been published by Jahn[2] on potassium chloride and sodium chloride at concentrations between 0.00167 and 0.033 molal and by MacInnes and Parker[3] on potassium chloride between 0.001 and 0.5 molal. The results of the last-named investigators give for the activity-coefficient of potassium chloride the values 0.653 at 0.5 molal, 0.738 at 0.1 molal, and 0.885 at 0.01 molal. The corresponding values

for hydrochloric acid presented in this article are 0.795, 0.844, and 0.945. The value (0.738) for potassium chloride at 0.1 molal is again much smaller (namely about 14% smaller) than the conductance-ratio (0.861).

A more complete description of this research will soon appear in the *Journal of the American Chemical Society*. The preparation of the cells so as to secure constancy and reproducibility of the electromotive force values, the methods of making the measurements, the full experimental data, and thermodynamic calculations from them of other free-energy values will be there presented in detail.

[1] Lewis, *Proc. Amer. Acad.*, **43**, 259–293 (1907); *Zs. physik. Chem.*, **61**, 129–165 (1908).
[2] Jahn, *Zs. physik. Chem.*, **33**, 545–576 (1900).
[3] MacInnes and Parker, *J. Amer. Chem. Soc.*, **37**, 1445–1461 (1915).

EFFECTS OF CENTRIFUGAL FORCE ON THE POLARITY OF THE EGG OF CREPIDULA

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If the eggs of the marine gasteropod Crepidula plana are subjected to centrifugal force of approximately two thousand times gravity the yolk is thrown to the distal or centrifugal pole, the oil and other light substances to the centripetal pole, while the nucleus and centrosphere together with most of the cytoplasm occupy the middle zone between the other two. In eggs centrifuged after fertilization and before the first cleavage the yolk zone comprises a little more than three-quarters of the volume of the whole egg, the middle zone a little less than one-quarter and the oil zone about one sixty-fourth, the relative volumes of the three being 49:14:1. In normal eggs of this stage the nucelus centrosphere and most of the cytoplasm lie near the animal pole, but in centrifuged eggs these formative substances may be displaced far from this position, the yolk, for example, being thrown to the animal pole and the protoplasm to the vegetative pole, or these displacements may take place in any other axis. Nevertheless these substances slowly come back to their normal positions provided there is sufficient time for this before the next cell division. However if cell division intervenes